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Radiofrequency-induced temperature increase as a function of cross polarization contact time in 8CB

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In this work we analyse the non-negligible heating effect that can be produced by the radiofrequency during the contact time in Hartmann–Hahn cross polarization experiments in liquid crystals. We perform the analysis in the nematic phase of 4-*n*-octyl-4′-cyanobiphenyl (8CB). The heating effect is quantified through the chemical shifts of the carbon resonances, which move towards their respective positions in the isotropic phase when increasing the contact time. The calibration procedure involves an independent measurement of chemical shift dependence on externally controlled bath temperature. This variation was performed in the range between 300 and 313 K covering the smectic A and nematic mesophases. An overall heating rate of 0.16 K ms^{-1} is observed during the contact time in a cross polarization experiment performed at $\omega_1/2\pi \simeq 80$ kHz. This rate goes to approximately one-half for $\omega_1/2\pi \simeq 60$ kHz and becomes unobservable for $\omega_1/2\pi < 50$ kHz under typical experimental conditions. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

It is a well known fact that the radiofrequency (r.f.) power used in standard nuclear magnetic resonance (NMR) experiments is able to produce heating effects in samples containing electrolytes or molecules with high permanent electric dipole moments. In particular, in liquid crystals of the 4-*n*-alkyl-4′-cyanobiphenyl series (electric dipole moment of approximately 14×10^{-30} C m)[1] this heating effect has been observed when acquiring ^{13}C NMR spectra with high-power ^{1}H decoupling. There, the need for long time irradiation during the acquisition period, usually longer than 40 ms, with high r.f. power leads to the mentioned effect.[1–3] At low frequencies, the orientation of the permanent dipoles follows the electric field. However, when the field is oscillating very fast, as in typical NMR experiments, the dipoles are not able to follow the field because of the increasingly important forces impeding the molecular reorientation. Thus, a phase lag is built up between the field and the dipoles, and the energy drawn from the electric source is dissipated as heat in the sample. Under this condition, the selection of the recycling time t_{rec} between FIDs for a particular ^{13}C NMR experiment is not trivial. It is not enough to set t_{rec} longer than

four or five times T_1 (where T_1 is the spin-lattice relaxation time for carbon) as usual, but it is necessary to wait for the complete thermal relaxation of the system. We have recently studied these slow processes through the behaviour of resonance positions and linewidths as function of t_{rec} in 5CB (unpublished results). However, the nuisance of the heating generated during ^{1}H decoupling can be circumvented by using sequences like TPPM, SPARC, and SPINAL, which reach the goal with much lower r.f. powers.[4,5] For these sequences, shorter recycling times are sufficient.

In this paper we analyse the r.f. heating process from a different point of view and on a different time scale. We show the effect of r.f. irradiation as a function of contact time in cross polarization (CP) experiments for a couple of r.f. powers. Multipulse sequences containing CP steps have been successfully applied to obtain order parameters and other detailed structural and dynamical information in liquid crystals. In particular, separated-local-field spectroscopy[6] or proton-detected-local-field experiments[7] and standard CP[8] experiments have been used with this purpose. Even though in the contact part of the experiment the r.f. is on only for short times (typically 2–5 ms), the application of the Hartmann–Hahn matching condition imposes a carbon field that is four times larger than the proton spin-lock field. The sensitive parameter we used to observe the r.f. heating during the contact time was the chemical shift of each line in the ^{13}C spectrum. Then, we observed that during the contact time the lines shift in the direction of their positions in the isotropic phase. The observation of this effect requires low r.f. power during the decoupling

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and long recycling times. This makes negligible the heating effect induced by irradiation during the acquisition and assures that the system returns to equilibrium, involving spin and thermal relaxation. It is under these conditions that one can clearly follow the behaviour of the chemical shift as a function of contact time and r.f. power. As above some r.f. power level the heating effect is not negligible, we want to emphasize its importance in multipulse sequences and multidimensional NMR experiments on electrolytes and systems with high electric dipole moments, including biological samples. Although this effect, if not properly treated, can produce artefacts in data analysis, it is interesting to note that it could be exploited to produce local heating in heterogeneous systems.

EXPERIMENTAL

The experiments have been carried out on 4-*n*-octyl-4'-cyanobiphenyl, also called 8CB (see Fig. 1) obtained from Sigma (Chemical, Co.) and used without further purification. This system presents the mesophases smectic A (SA) and nematic (N), with transitions at 306.5 K (SA-N) and 313.5 K (N-I).

In order to quantify the heating effect, we have measured the temperature dependence of the ^{13}C chemical shift from 300 K up to the nematic isotropic transition temperature (T_{NI}). These 8CB spectra were taken using a Bruker DSX-500 with a standard CP-MAS probe containing 4 mm o.d. rotors under static conditions and controlled temperature. During the contact time $\tau_C = 2$ ms, the Hartmann–Hahn condition was set at a frequency $\omega_1/2\pi = 60.3$ kHz. In these experiments, the CP sequence was combined with SPINAL-64[5] for decoupling during acquisition ($t_{AQ} = 74$ ms). A time $t_{rec} = 15$ s was left between FIDs after checking that with the use of SPINAL-64 no dependence is observed on t_{rec} for $t_{rec} > 12$ s. Thus, this delay assures the return to equilibrium even for the slowest thermal processes. In addition, an appreciable resolution enhancement was achieved in comparison with spectra taken under high-power decoupling, in complete agreement with the work by Fung *et al.*,[5] where SPINAL-64 was shown to be the best among several decoupling sequences applied to liquid crystals. A very long time of approximately 30 min was left after an increment of 1 K with the temperature control unit of the spectrometer. Two CP experiments as a function of τ_C were performed in the nematic phase at 311.5 K, with $4 \mu s < \tau_C < 3.5$ ms, using SPINAL-64 for decoupling ($t_{AQ} = 74$ ms) with $t_{rec} = 15$ s. In one of them the H–H condition was set with $\omega_1/2\pi = 80.6$ kHz, whereas in the other it was $\omega_1/2\pi = 60.3$ kHz. In both experiments
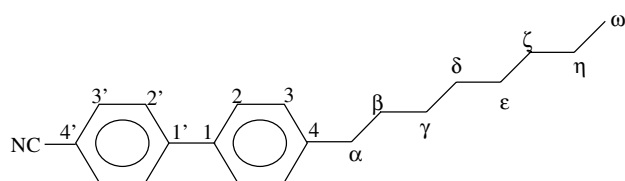

Figure 1. Chemical structure of 8CB showing the labels used in the ^{13}C NMR spectra.

we analysed the behaviour of the chemical shifts versus contact time. In all these experiments the temperatures were calibrated using the N-I temperature transition. A ^{13}C NMR spectrum of 8CB in the isotropic phase (at 320 K) was taken as a reference using a single pulse sequence with ^{1}H decoupling (direct ^{13}C polarization).

RESULTS AND DISCUSSION

The ^{13}C NMR spectra of 8CB in different phases can be seen in Fig. 2. The assignments of the lines in the isotropic phase have been made using the Advanced Chemistry Development (ACD) program. We have taken as reference the theoretical position given by the ACD program for the ω carbon (methyl group) in the isotropic phase (14.1 ppm). Although this may not be completely accurate, we are not interested in the exact values of chemical shifts in this study, only in their relative shifts with temperature. In the nematic and smectic phases, peak assignments of the aromatic carbon atoms were given in previous studies.[9] Although we do not have an unambiguous criterion to distinguish the signals from C(4) and C(1'), we follow the recent study by Fung *et al.* in 5CB, where previous assignments were corrected.[5] Though there are several reports of the ^{13}C chemical shifts of 8CB[10] for carbon atoms in the aliphatic chain, this is, to our knowledge, the first time that seven of the eight lines have been resolved in both the nematic and smectic phases. Hence, tentative assignments have been made by comparing the order parameters (unpublished results) evaluated from the behaviour of the carbon magnetization versus contact time in the CP experiments[8,11] with those obtained theoretically and by using deuterium NMR.[12,13] In those studies, theoretical models involving several conformers of the alkyl chains were in excellent agreement with segmental order parameters obtained from deuterium NMR experiments.

In Fig. 3 we can see the behaviour of the chemical shifts as a function of temperature from 301.5 K up to T_{NI}. For practical reasons, in the systematic analysis we obtained the chemical shifts from power spectra, but no appreciable differences occur if corrected phase spectra are used. The first observation is that all the ^{13}C signals shift with temperature going towards their positions in the isotropic phase as temperature increases. Thus, the aromatic carbon lines decrease in the ppm scale and the aliphatic carbon lines increase. The overall shift is larger for aromatic carbon atoms than for aliphatic carbon due to their more important chemical shift anisotropy, which is increasingly averaged by motion. However, even the more mobile groups in the aliphatic chain (C(ς), C(ω)) give an appreciable variation when the temperature approaches T_{NI}. It is also possible to see a signal that is only present for temperatures above 307.5 K. This signal corresponds to the widest resonance in the nematic spectrum of Fig. 2. Because of the high frequency of its transient oscillation as a function of contact time in a CP experiment,[11] revealing a high residual ^{13}C–^{1}H dipolar interaction, we have assigned this signal to the α carbon C(α). The broadening of this line compared with those of the other aliphatic carbon atoms can be assigned to the slow motions of C(α), which, being attached to the biphenyl group
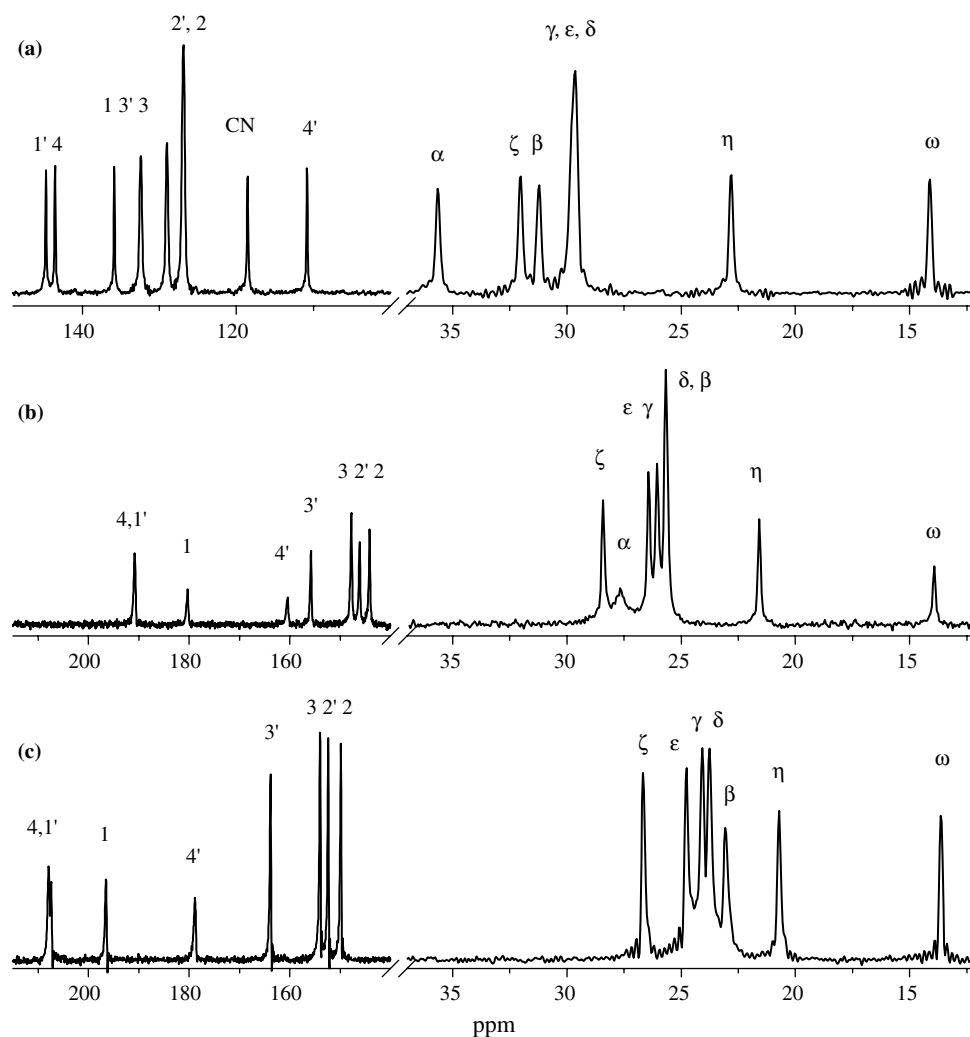
Figure 2. ^{13}C NMR spectra of 8CB in (a) the isotropic phase at 320 K, (b) the nematic phase at 311.5 K and (c) smectic phase at 300 K. The tentative assignments for the nematic and smectic phases have been made by comparing the experimental order parameters with theoretical order parameters (see text). For labels, refer to Fig. 1.

(or core), has fewer degrees of freedom and conformation possibilities than the other carbon atoms of the chain. Thus, it seems that, in the nematic phase, C(α) explores different orientations but the motion is not fast enough to produce motional narrowing. This regime is, of course, reached in the isotropic phase, where, as can be observed in Fig. 2, the linewidths of all the lines corresponding to aliphatic carbon atoms are approximately equal. We can also see in Fig. 3 that the lines in the aromatic carbon atoms remain parallel (they do not cross) as the temperature increases. In contrast, we can see that C(δ) and C(β) merge at 309.5 K (and this group of lines remains parallel to C(ε) and C(γ)); we also assume that C(α) overlaps with the group of lines formed by C(ε)–C(β) for temperatures below 307.5 K. The variation of the chemical shift with increasing temperature helped us to assign the resonances of the aliphatic carbon atoms.

It is worthwhile observing that a *jump* occurs in all the line positions at a temperature that can be identified with the smectic–nematic transition. The amplitude of this jump is between 1 and 2 ppm for the aromatic carbon atoms and about 0.5 ppm for carbon atoms C(ζ)–C(β). The fact that no ^{13}C spectrum could be obtained using CP above 313.5 K

tells us that the system is already in the isotropic phase. The spectrum can then be easily obtained by direct ^{13}C measurement.

We have analysed the variation of chemical shift versus temperature in three different regions: 301.5–305.5 K (part **I**), 306.5–310.5 K (part **II**) and 311.5–313.5 K (part **III**). In Fig. 3 we can appreciate that the variation of chemical shift with temperature is more important as temperature increases, and accelerates near T_{NI}. The fact that the carbon atoms of the aromatic part are more sensitive to temperature changes than the aliphatic carbon atoms can be seen directly or by comparing the slopes obtained from the fits. For example, in region **I** the aromatic carbon atoms have slopes falling in the interval [−1.0, −0.29] ppm K^{-1}, whereas those for carbon atoms in the chain are in the interval [0.056, 0.145] ppm K^{-1}. The difference in the behaviour is attributed to the lower anisotropy and high mobility of carbon atoms β to ω, already present in the smectic phase, giving further averaging and less sensitivity to temperature.
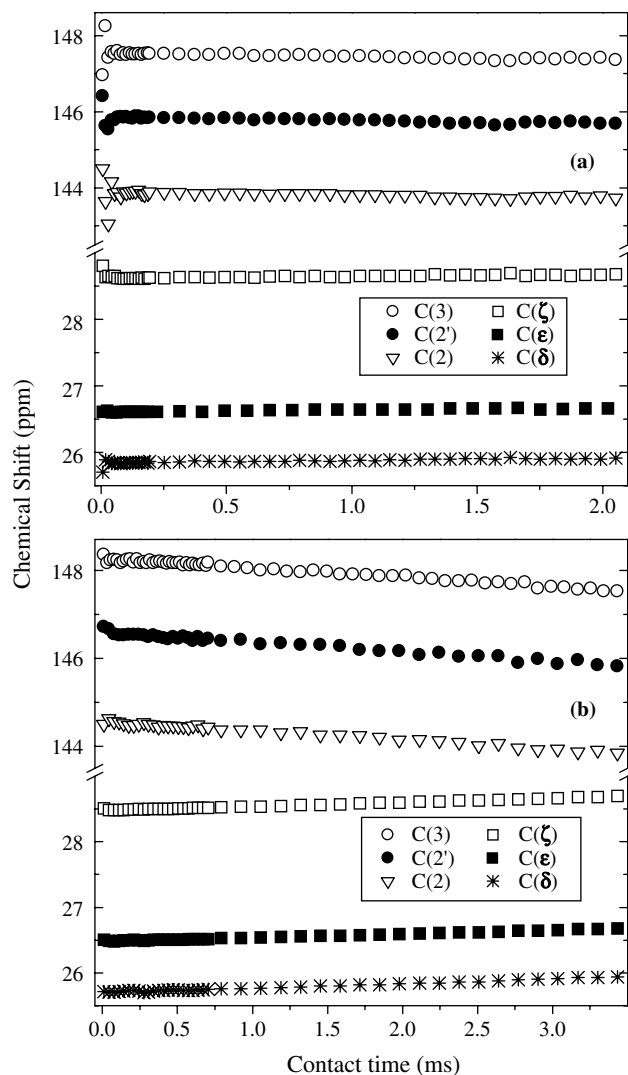
In Fig. 4a and b we show the variation of the ^{13}C chemical shifts versus τ_C in the CP experiments performed in the nematic phase. In both cases we can see a more
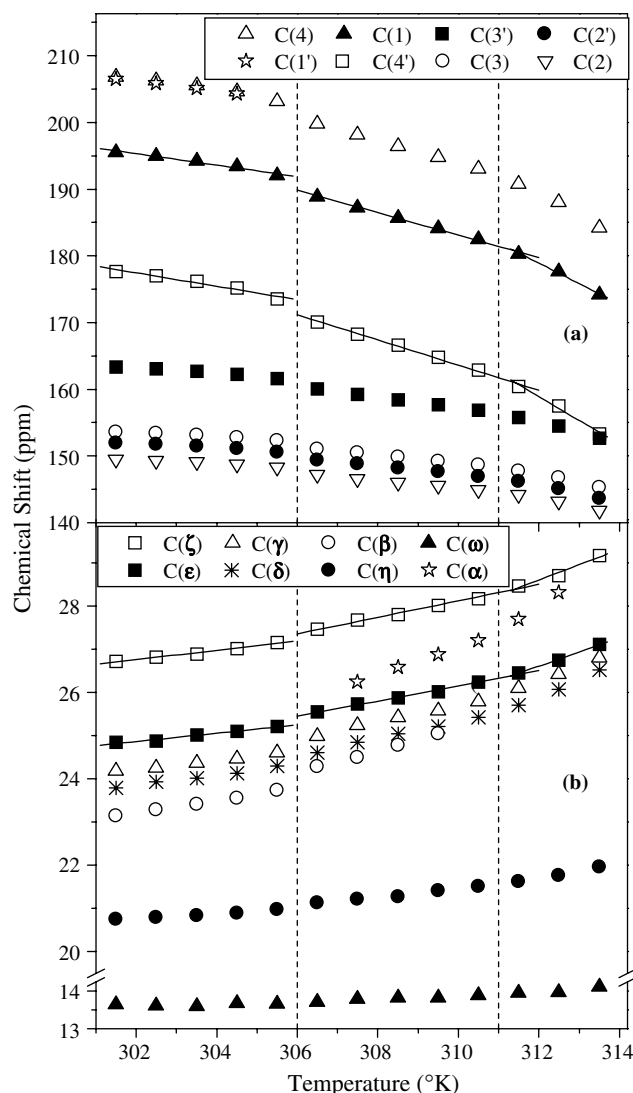
Figure 3. Chemical shifts as a function of temperature for (a) the aromatic carbon atoms and (b) aliphatic carbon atoms. We can see some representative fits in both graphs. Note the jump that occurs at the smectic–nematic transition temperature. For a better visualization of the temperature dependence, the graph has been separated into parts **I**, **II** and **III**: 301.5–305.5 K, 306.5–310.5 K and 311.5–313.5 K respectively.

Figure 4. Chemical shifts as a function of the contact time in a Hartmann–Hahn CP experiment with (a) $\omega_1/2\pi = 60.3$ kHz and (b) $\omega_1/2\pi = 80.6$ kHz. The behaviours of representative carbon atoms in the aromatic and aliphatic parts of the molecule are displayed. For the labels of the carbon atoms, refer to those in Fig. 1.

pronounced variation for the aromatic carbon atoms. By comparing the slopes obtained from linear fits to the data in the CP experiment at $\omega_1/2\pi = 60.3$ kHz with those from the experiment at $\omega_1/2\pi = 80.6$ kHz, we see that the rate of variation of chemical shift per millisecond in the former case is about one-half that for the latter. More precisely, the slopes of variation for aromatic carbon atoms in the 80.6 kHz experiment are in the interval $[-0.52, -0.198]$ ppm ms^{-1}, whereas in the 60.3 kHz case they fall in the interval $[-0.26, -0.076]$ ppm ms^{-1}.

It is interesting to mention that when using settings where $\omega_1/2\pi < 50$ kHz we could not observe any appreciable heating. Also, in a CP experiment in the smectic phase using $\omega_1/2\pi \approx 60$ kHz, the more important variation we could observe was in C(4) with a variation of -0.05 ppm ms^{-1}. This

is because, as shown in Fig. 3, the temperature dependence of the chemical shifts in the smectic phase is less pronounced than in the nematic phase.

Finally, in Table 1 we show the temperature variation versus contact time for both CP experiments in nematics; these results have been obtained by combining our linear fits of chemical shift versus temperature (for part **III**) with the chemical shift versus contact time. Note that in both experiments all the lines point to the same rate, i.e. the increment of temperature for carbon atoms in the chain is the same, within experimental error, as for carbon atoms in the aromatic part. This fact allows us to establish an average homogeneous increment of temperature of the sample during the contact time in a CP experiment. These increments are about 0.16 ± 0.02 K ms^{-1} for the experiment at $\omega_1/2\pi = 80.6$ kHz and 0.074 ± 0.008 K ms^{-1} (this average does not include the values from C(η), C(ω)) for that at $\omega_1/2\pi = 60.3$ kHz. Taking into account the accepted

Table 1. Rate of variation of the temperature versus contact time in two CP experiments with a temperature setting at 311.5 K[a]

	CP, $\omega_1/2\pi = 60.3$ kHz (K ms^{-1})	CP, $\omega_1/2\pi = 80.6$ kHz (K ms^{-1})
C(4)	0.069 ± 0.009	0.16 ± 0.02
C(1)	0.069 ± 0.009	0.15 ± 0.03
C(4′)	0.07 ± 0.01	0.12 ± 0.03
C(3′)	0.07 ± 0.01	0.17 ± 0.02
C(3)	0.068 ± 0.01	0.17 ± 0.02
C(2′)	0.069 ± 0.009	0.17 ± 0.01
C(2)	0.065 ± 0.009	0.17 ± 0.01
C(ζ)	0.08 ± 0.02	0.17 ± 0.04
C(ε)	0.083 ± 0.009	0.17 ± 0.01
C(γ)	0.089 ± 0.007	0.182 ± 0.009
C(δ)	0.087 ± 0.008	0.16 ± 0.01
C(η)	0.14 ± 0.08	0.3 ± 0.2
C(ω)		0.022 ± 0.002

[a] The resonances of C(β) and C(1′) are not resolved at this temperature. The values from C(η) and C(ω) have very large errors because their chemical shifts depend very slightly on temperature. The resonance corresponding to C(α) is too broad to give good peak-picking. The errors shown in this table are the fitting errors.

mechanism of heating,[3] we can consider that essentially all the energy of the r.f. in the volume of the sample is dissipated as heat. Then, we should expect a temperature increase proportional to the square of the electric field. This leads us to a factor of 1.8 for the rate of temperature increase per millisecond between the two experiments, in good agreement with the value of two obtained experimentally with approximately 10% error (see Table 1). In our reasoning, we have neglected any contribution to the heating arising from the coil. This is completely justified in the time regime of study (<3 ms), because of the slow thermal diffusivity of the sample.

CONCLUSIONS

In this short article we have shown the non-negligible heating effect that the r.f. can produce on a liquid crystal sample with high electric dipole moment, even when applied for few milliseconds. This is particularly important for multipulse

sequences containing CP steps or spin-locks in carbon nuclei, as in the sequence to observe polarization echoes.[14,15] In some cases, the heating problem can be circumvented by using other polarization transfer procedures, such as via the NOE, where ^{13}C irradiation is not required. However, when the dynamics of the coherent transfer occurring in the presence of a strong heteronuclear interaction is the effect to be exploited,[11] the CP step cannot be avoided.[8] From a practical point of view, care must be taken with the shifts of the signals as a function of ^{13}C irradiation time, especially when using automated programs of analysis. Given the time regime of our study, it should be absolutely clear that this heating has nothing to do with either the spin–lattice relaxation of the Zeeman magnetic energy, which in any case is negligible, or with the heating of the coil itself. This latter effect should show a delay proportional to the thermal conductivity of the sample, which for this series of liquid crystals involves the order of seconds per millimetre.

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